

Photoinduced C_{70} radical anions in polymer:fullerene blends

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Photoinduced polarons in solid films of polymer–fullerene blends were studied by photoluminescence (PL), photoinduced absorption (PIA) and electron spin resonance (ESR). The donor materials used were P3HT and MEH-PPV. As acceptors we employed $PC_{60}BM$ as reference and various soluble C_{70} -derivates: $PC_{70}BM$, two different diphenylmethano-[70]fullerene oligoether (C_{70} -DPM-OE) and two dimers, C_{70} - C_{70} and C_{60} - C_{70} . Blend films containing C_{70} revealed characteristic spectroscopic signatures not seen with C_{60} . Light-induced ESR showed signals at $g \geq 2.005$, assigned to an electron localized on the C_{70} cage. The formation of C_{70} radical anions also leads to a subgap PIA band at 0.92 eV, hidden in the spectra of C_{70} -based P3HT and MEH-PPV blends, which allows for more exact studies of charge separated states in conjugated polymer: C_{70} blends.

Keywords: Electron Spin Resonance, Photoinduced Absorption, Fullerene, C_{70}

Due to their potentially low manufacturing costs, thin film organic solar cells (OSC) may become highly competitive in the area of direct solar energy conversion. Efficiencies of 8.3 % have already been reported^{1,2}. For directed optimization efforts a better understanding of the photophysical processes in the device during the conversion of incident light into electrical energy is required. Using blends of conjugated polymers and fullerenes, an efficient photoinduced charge separation can be achieved, subsequently followed by migration of the charges to the device electrodes. $PC_{60}BM$, a soluble fullerene derivative, is used as acceptor material in the vast majority of the OSC devices reported. It was outperformed recently by $PC_{70}BM$, due to its higher absorption coefficient in the visible part of the solar spectrum (figure 1), but also due to the slightly higher open circuit voltage^{3,4}.

Although understanding of the elementary steps of efficient charge separation in the photovoltaic materials is a prerequisite for improving the efficiency, the photophysics of C_{70} containing blends is much less investigated than its C_{60} relatives. So far ESR and VIS-NIR spectra of C_{70} derivates obtained in different phases like crystallites, salt-like samples and dilute (frozen) solutions in (un)polar solvents were previously presented in the literature^{5–8}. The resulting signals differ for each different phase, due to interaction with the host material. Therefore from the ESR measurements the undisturbed g -tensor components of the C_{70} radical anion could not be obtained. Additionally several partly overlapping NIR-absorption bands of single and multiply charged C_{70} an-

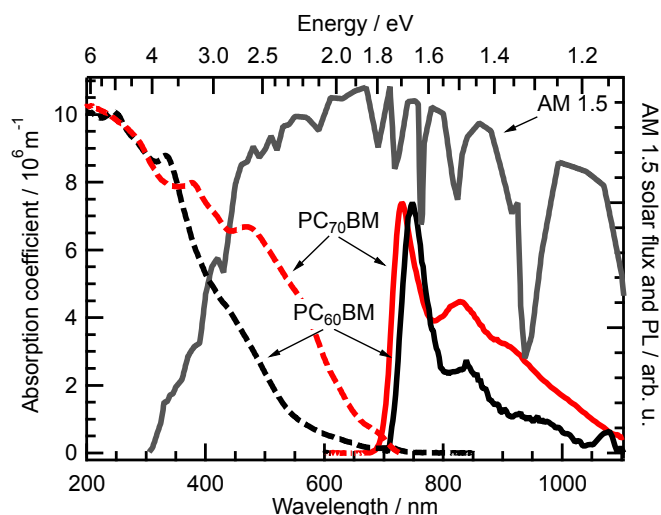


Figure 1: AM 1.5 solar flux (normalized), absorption at 300 K (dashed) and normalized PL at 12 K (solid) of thin films of $PC_{60}BM$ (black) and $PC_{70}BM$ (red).

ions and cations were detected. An absorption at 1370 nm (0.905 eV) was tentatively assigned to solvation complexes of C_{70} radical anions in solution^{5,7}. Recently, we reported on new C_{70} -based fullerene dimers showing additional PIA and ESR features when blended with conjugated polymers in thin solid films⁹. We investigated the symmetry of the resulting g -tensor in polymer: C_{70} blends¹⁰. Here we generalize these findings for a broader class of C_{70} fullerene derivates in solid state and present results of the subgap PIA determining the excitation energies of the involved excited state.

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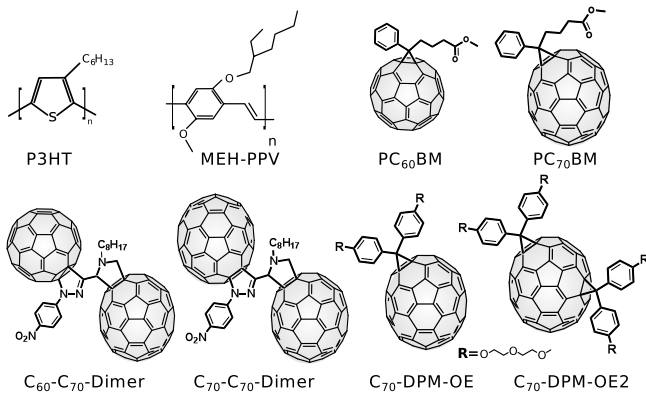


Figure 2: Donor-polymers P3HT and MEH-PPV. Employed acceptors were C₇₀ fullerene derivatives and PC₆₀BM as reference.

P3HT (Rieke Metals), MEH-PPV (Sigma-Aldrich), PC₆₀BM and PC₇₀BM (Solenne B.V.) were used as purchased. Details about the synthesis of the fullerene dimers and C₇₀-DPM-OE are reported elsewhere⁹. Samples were processed from chlorobenzene solutions (10 mg/ml) with a 1:1 weight ratio for blends. Thin films of ~ 100 nm were spincoated onto sapphire substrates for use in PIA, PL and absorption. For ESR 200 μ l solution were vacuum-dried inside an ESR sample tube. All samples were annealed afterwards for 10 min at 130 °C.

Figure 1 shows that PC₇₀BM has an increased absorption in the range of 400–700 nm compared to PC₆₀BM, which is favorable in view of the AM 1.5 solar flux. Absorption was measured with a Perkin-Elmer Lambda 900 spectrometer under ambient conditions. At low temperatures (12 K) these samples emitted a weak, yet detectable PL when excited by a 532 nm laser. Intensities of the PL spectra were corrected for the spectral response of the spectrometer. The spectra of both fullerene derivatives showed well resolved vibronic structures and the PL of PC₇₀BM was blue-shifted by ~ 40 meV (17 nm) matching literature values¹¹.

In figure 3 (left) the light-induced ESR spectra (normalized) of P3HT blended with the different fullerene derivatives are shown. Illumination was provided by a 532 nm laser and the samples were cooled to 100 K. All spectra exhibit the typical derivative-like absorption line at $g=2.002$, originating from positive polarons on the polymer chain. In P3HT:PC₆₀BM blends, the radical anion of C₆₀ can be detected at $g=2.000$. For blends consisting of P3HT and C₇₀-derivatives no such signal can be identified directly, as the C₇₀ radical anion line is strongly superimposed with the polymer polaron signal. Instead all C₇₀-containing blends disclose a shoulder at $g \geq 2.005$, being absent in the spectrum of P3HT:PC₆₀BM. In figure 3 (right), the deconvolution of the experimental spectra into their contributions of the positive polymer polaron, the C₇₀ (top) and C₆₀ (bottom) radical anion are shown. The deconvolution method has been described elsewhere¹⁰. We were able to simulate the spectra of the fullerene-anions (using Simfonia) with the following g -tensor components ($g_{xx}/g_{yy}/g_{zz}$): C₆₀⁻ = (2.00058/2.00045/1.99845) and C₇₀⁻ = (2.00592/2.00277/2.00211). A closer look at the spectrum

of P3HT:C₆₀-C₇₀-dimer (e) revealed, that contributions of both fullerene anions are present, hinting that the charge transfer process is not dominated by one fullerene.

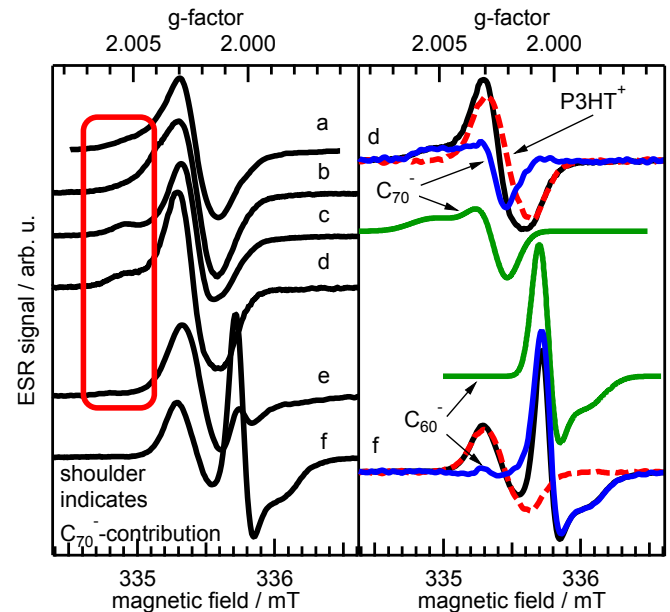


Figure 3: Left side: ESR spectra at 100 K of P3HT blended with different fullerenes: C₇₀-C₇₀-Dimer (a), C₇₀-DPM-OE2 (b), C₇₀-DPM-OE (c), PC₇₀BM (d), C₆₀-C₇₀-Dimer (e), PC₆₀BM (f). All C₇₀-composites show a shoulder for $g \geq 2.005$ (indicated by the red rectangle) which is assigned to the C₇₀ anion. Right side: Deconvolution of the experimental spectra (black), the positive polaron P3HT⁺ (dashed red), the fullerene anions (blue) and their simulated spectra (green) for composites (d) and (f).

Further, we studied the photophysical properties by photoinduced absorption (PIA). The excitation by a 532 nm laser leads to singlet excitons, which are separated at the polymer:fullerene interface yielding positive and negative charge carriers in the polymer and the fullerene phase, respectively. The resulting change in transmission of a white light continuum probe beam was measured ($-\Delta T/T$). The transmitted light was focussed into a monochromator and the detection was provided by a silicon photodiode (550–1030 nm) and a liquid nitrogen cooled InSb-detector (1030–5500 nm). In most polymer:fullerene blends, transitions ascribed to polaronic states (radical cations) are located at 0.3 eV and 1.2 eV. For P3HT or PPV blended with PC₆₀BM these spectral signatures are well documented^{12,13}.

In the PIA spectra of all polymer:C₇₀ blends, similar polaronic absorption bands could be detected, indicating efficient charge separation. Additionally we found an absorption at 0.92 eV (figure 4), which is absent in the reference P3HT:PC₆₀BM spectrum and therefore related to the C₇₀. As the examined fullerene derivatives have different side chains, we can exclude electrons being localized on here. Charge transfer states as possible candidates for a new subgap absorption could be ruled out by replacing the host polymer P3HT with MEH-PPV, which has different HOMO-LUMO energies^{14,15}. Furthermore the relation of the 0.92 eV peak

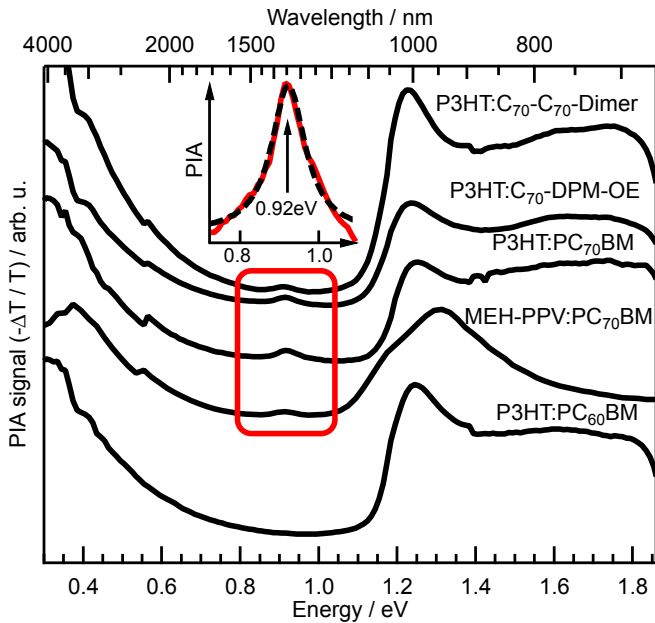


Figure 4: PIA spectra at 15–30 K. While the structure of the spectra is similar, the peak at 0.92 eV shows up only in blends with C_{70} -derivates. **Inset:** Subtraction (red) of the normalized spectra of P3HT:PC₆₀BM from P3HT:PC₇₀BM together with a Lorentzian fit of the lineshape (dashed black).

to C_{70} -derivatives is also consistent with the different temperature dependence of the PIA peaks in the blend of MEH-PPV:PC₇₀BM (data not shown). The polaron peaks at 0.3 eV and 1.2 eV show both an identical decrease in signal intensity when increasing the temperature from 30 K to 300 K,

while the 0.92 eV peak decreases steeper and vanishes at 300 K. We were able to separate the contribution of the underlying peak by subtracting the normalized spectrum of P3HT:PC₆₀BM from P3HT:PC₇₀BM. This is shown together with a Lorentzian fit of the spectrum in the inset in figure 4 ($E_0 = 0.92$ eV / 1350 nm and FWHM = 0.11 eV).

To summarize, we have studied a variety of solid films of C_{70} -fullerene derivatives and dimers blended with two different conjugated polymers, with the emphasis on the photogenerated radical anion. We identified spectral features originating from C_{70} in PIA and ESR spectroscopy, namely an additional subgap PIA peak at 0.92 eV and an ESR-shoulder at $g \geq 2.005$. By comparing results from different blends we can infer that these features are indeed signatures of the C_{70} radical anion and not originating from the side chains of the fullerenes or charge transfer states at polymer: C_{70} -fullerene interfaces. As anticipated, ESR signatures related to the C_{70} radical anion were found and the corresponding spectra could be simulated with the g -values from our previous findings¹⁰. The obtained signatures are of importance for studying the charge transfer reactions in C_{70} -based bulk-heterojunctions.

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